How Classical is Nucleation?

With:
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Outline

We use simulations to test

1. Classical Nucleation Theory
2. Ostwald’s rule
3. Alexander-McTague rule
4. Turnbull’s rule
5. The “nucleation theorem”

...and find a few surprises.

Intermezzo:

Why Ostwald would have disagreed with this talk.

I am a molecular simulator.. But Ostwald did not believe * in the reality of atoms:

"Only energy is real – believing in atoms is like worshipping idols…"

W. Ostwald

* But after Perrin's experiments on colloids, Ostwald was "converted"

Why do I defy Ostwald?

Simulations tell us things about nucleation that experiments cannot tell us…

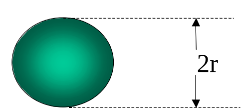
…yet

Homogeneous nucleation

(e.g. Liquid ⇒Solid)

Crystallization requires supercooling

$(\mu_{solid} < \mu_{liquid})$



Crystal nucleus

Free - energy gain

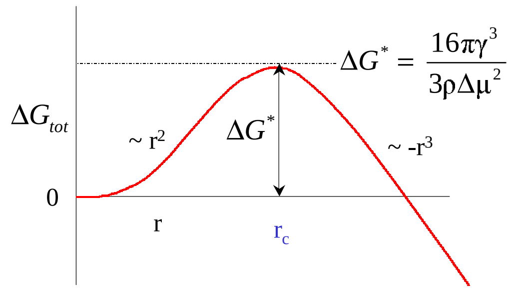
$$\Delta G_{Bulk} = \frac{4\pi}{3}\rho r^{3}\Delta\mu_{s,l} < 0$$

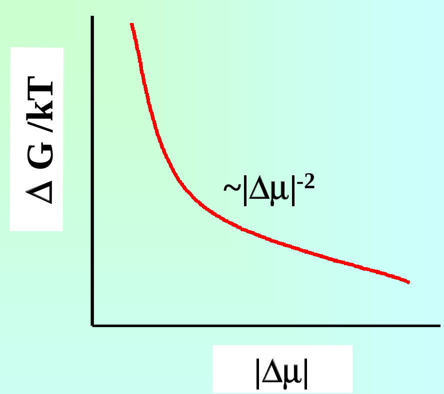
Free - energy loss :

$$\Delta G_{Surface} = 4\pi r^{2}\gamma_{s,l} > 0$$

r^3

r^2





According to CNT:

Barrier decreases monotonically with $|\Delta\mu|$

What does this imply for simulation?

Consider "realistic" supercooling

(10%-20%)

Experimental nucleation rates:

$\mathcal{O}(1)$ cm^{-3} s^{-1}

Simulation:

Volume is much smaller (e.g. for one million particles): V= $\mathcal{O}(10^{-15})$ cm^{3}

⇒Nucleation rate is $\mathcal{O}(10^{-15})$ s^{-1} !!

⇒One event per **10^{15} s**

⇒One event per **10^{30} MD time steps**

BRUTE FORCE WON'T WORK...

Solution:

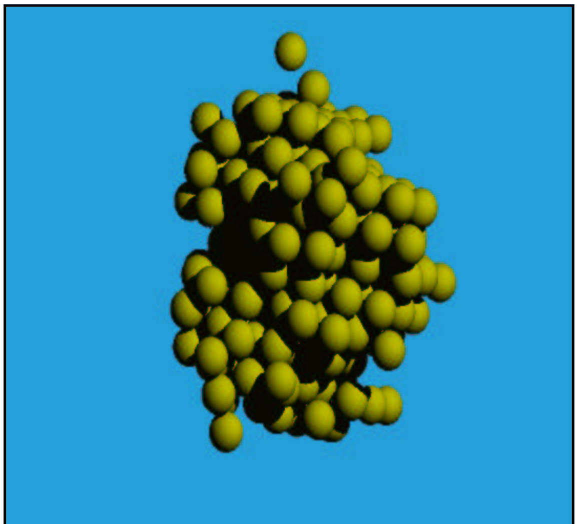
1. **Compute height of the free-energy barrier ΔG^* (MC/MD)**
2. **Compute transmission coefficient Γ (MD)**

$$\text{Rate} = \Gamma \; \exp(-\beta \Delta G^*)$$

Probability of "critical" fluctuation

(strong function of T)

Kinetic Prefactor
(usually weak function of T)



Critical crystal nucleus of hard-sphere colloids

Ostwald's Rule(1897)

"The phase that nucleates need not be the **stable** phase, but the one that is **closest in free energy** to the parent phase..."

Stranski & Totomanov (1930's)

"The phase that nucleates is the one with the **lowest nucleation barrier..**"

Alexander & McTague (80)

"On basis of Landau theory, one would expect the following crystal phases to form easily from the melt:

1. **Hexagonal** **(2D crystal)**
2. **Icosahedral** **(...)**
3. **BCC crystal**

Examples:

1. **Condensation of polar liquids**
2. **"Protein" crystallization**
3. **Crystallization of Charged colloids**

Experimental observation:

Classical Nucleation Theory works well for non-polar molecules **(e.g. CH_4)...**

... but not for polar molecules

(e.g. CH_3CN)

Why???

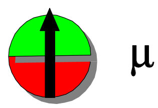
Experiments ...

...cannot probe the critical nucleus

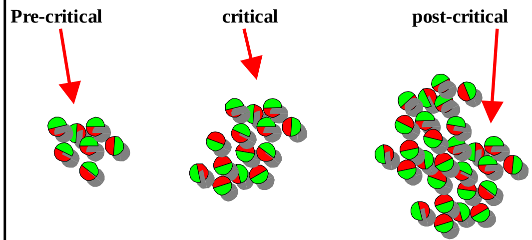
SIMULATION:

Stockmayer fluid

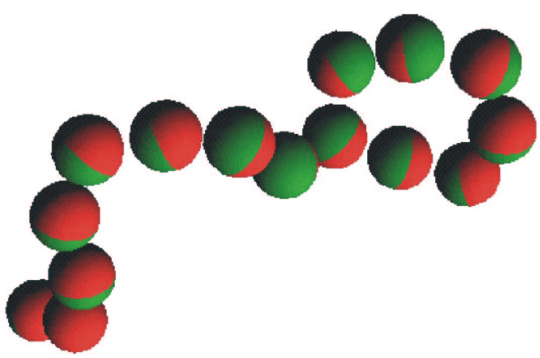
(= Lennard-Jones + embedded dipole)



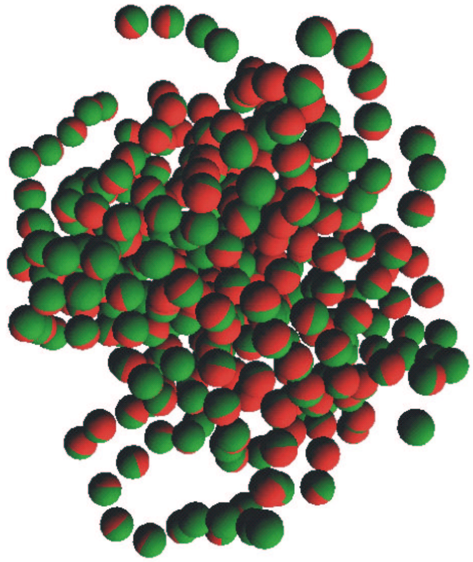
WHAT DO WE EXPECT TO SEE?



Pre-critical Nucleus



Critical Nucleus



NOT OSTWALD'S RULE

PRE-CRITICAL NUCLEI

⇓⇑

META-STABLE PHASE

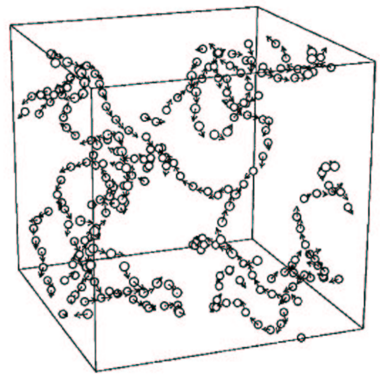
(Van Leeuwen & Smit, Caillol & Weis)

CRITICAL NUCLEUS:

Surface resembles

META-STABLE PHASE

What meta-stable phase??



"Gel" phase of dipolar hard spheres

Camp, Shelley, Patey, PRL 88,115(1999)

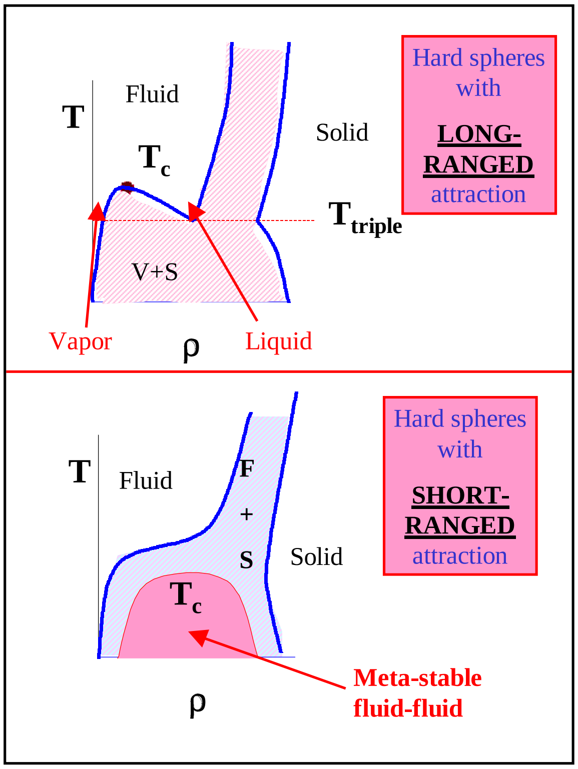
This is NOT a stable phase of the Stockmayer fluid.

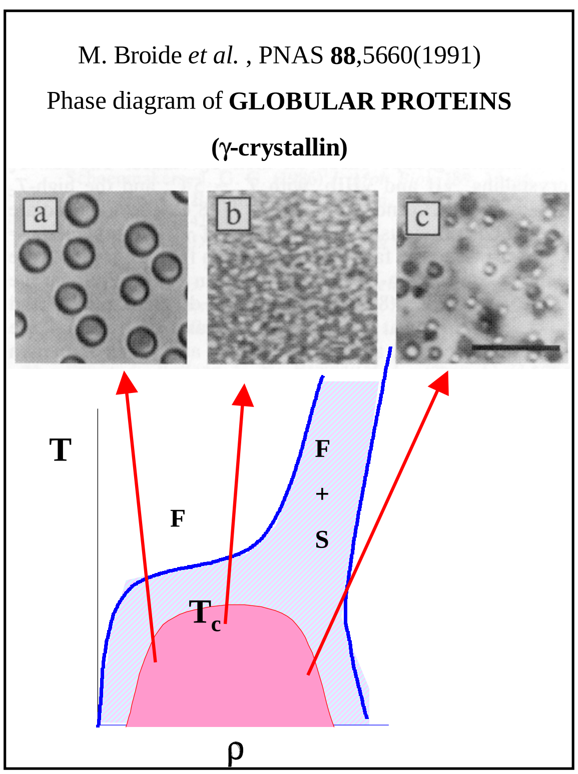
Crystallization of globular proteins

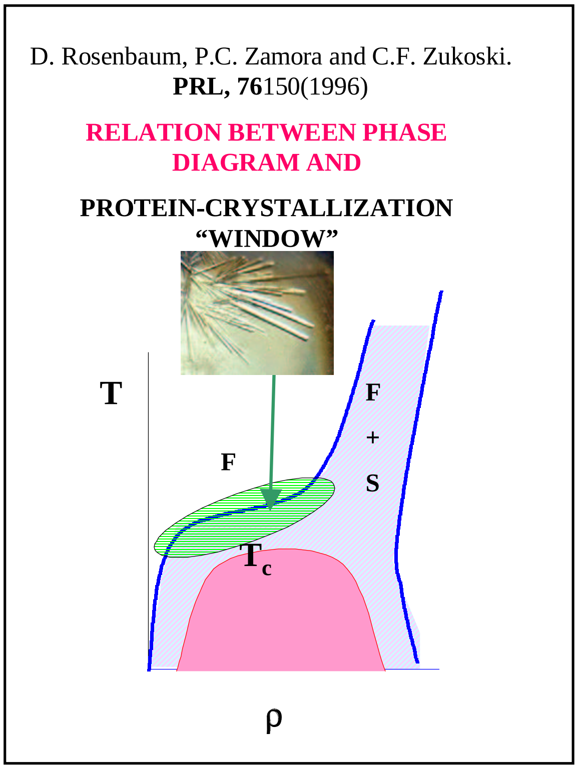
QUOTE:

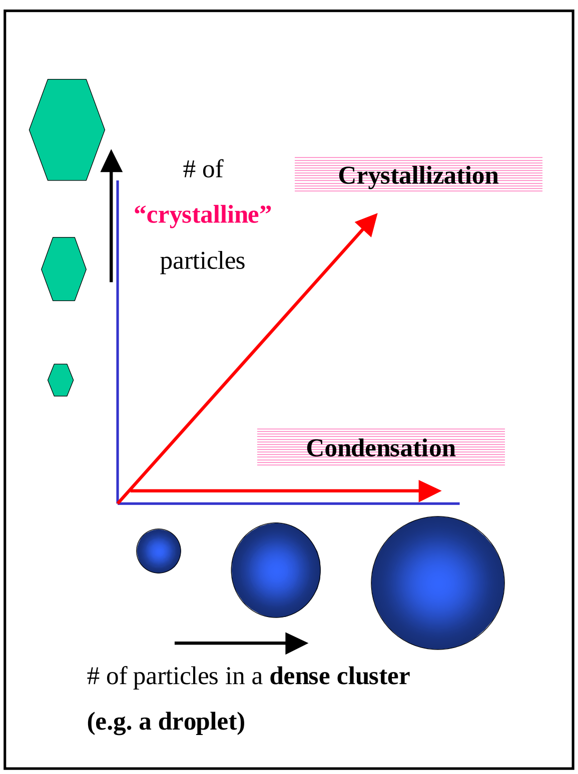
"... mainly trial and error... much like prospecting for gold..."

(McPherson "Preparation and Analysis of Protein Crystals")


Hard spheres with
LONG-RANGED
attraction
Fluid
Solid
T
T_c
T_{triple}
V+S
Vapor
ρ
Liquid
Hard spheres with
SHORT-RANGED
attraction
T
Fluid
F
+
S
Solid
T_c
ρ
Meta-stable
fluid-fluid

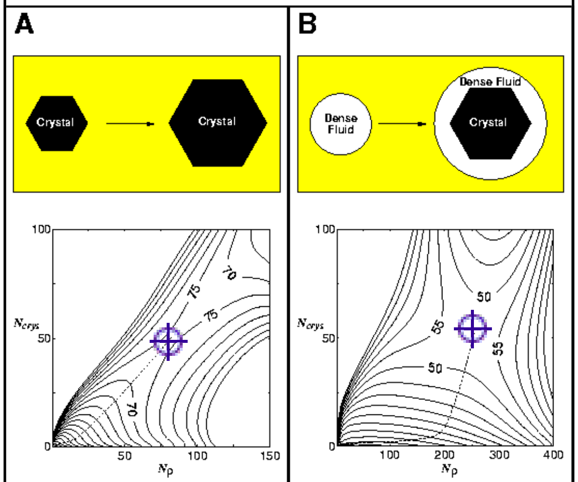

M. Broide *et al.* , PNAS **88**,5660(1991)
Phase diagram of **GLOBULAR PROTEINS**
(γ-crystallin)
a
b
c
T
F
F
+
S
T_c
ρ

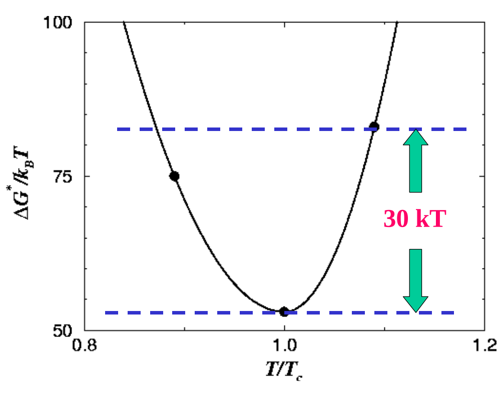

D. Rosenbaum, P.C. Zamora and C.F. Zukoski.
PRL, 76150(1996)
RELATION BETWEEN PHASE DIAGRAM AND
PROTEIN-CRYSTALLIZATION "WINDOW"
T
F
F
+
S
T_c
ρ


of
"crystalline"
particles
Crystallization
Condensation
# of particles in a dense cluster
(e.g. a droplet)

P.R. ten Wolde & D.F.

SCIENCE, **277**,1975(1997)



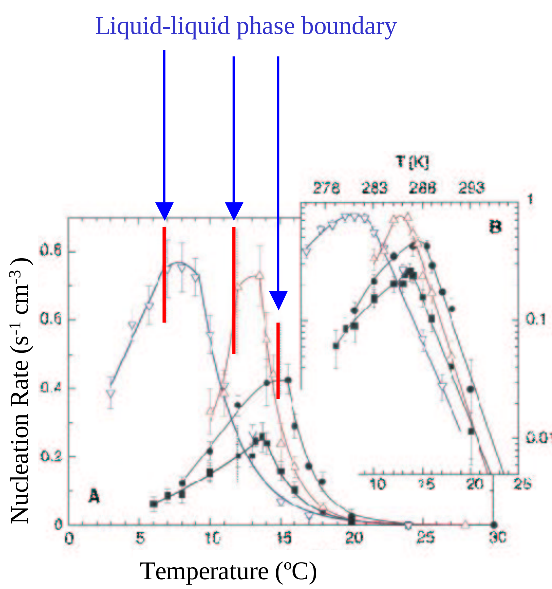


Experimental Evidence??

Recent experiments by Galkin and Vekilov

PNAS 97, 6277–6281(2000)

Lyzosyme crystallization



PRE-CRITICAL NUCLEI

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META-STABLE PHASE (Dense fluid)

CRITICAL NUCLEUS:

Surface resembles

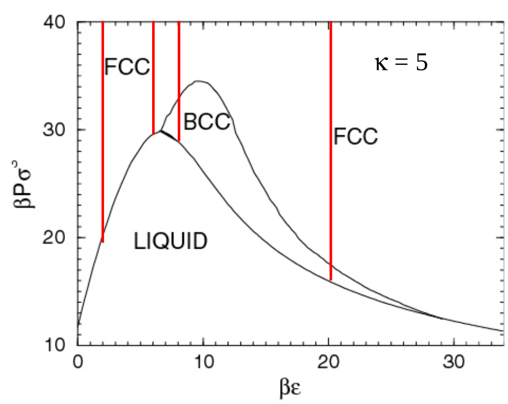
META-STABLE PHASE

Phase diagram of

Hard-core Yukawa model

(“charged colloids”)

v(r) = ε(σ/r) exp(-κ {(r/σ)-1})	(r/σ) ≥1
v(r) = ∞	(r/σ)<1



Ostwald

vs

Alexander-McTague

Ostwald:

When FCC is stable, nucleus should be BCC

When BCC is stable, nucleus should be FCC

Alexander-McTague

When FCC is stable, nucleus should be BCC

When BCC is stable,

…nucleus should also be BCC

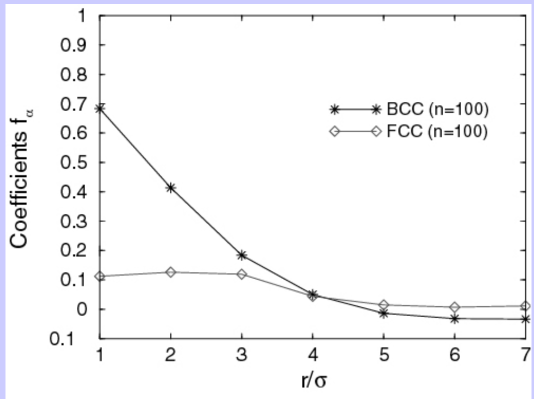
Simulations

Small nuclei are ALWAYS predominantly BCC

Large nuclei may be FCC or BCC, depending on which phase is stable

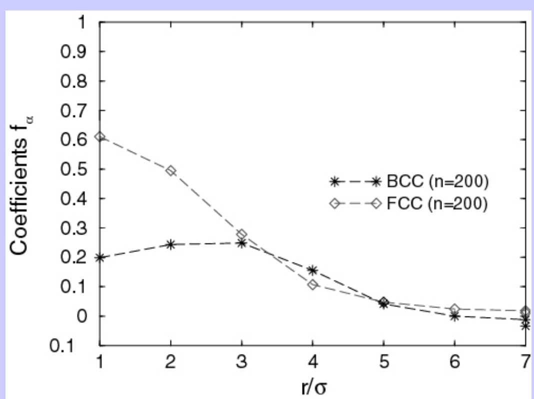
Simulations

(FCC stable)



Simulations

(FCC stable)



COMPARISON WITH EXPERIMENTS

AND

TESTING CLASSICAL NUCLEATION THEORY

TEST CASE

CRYSTAL NUCLEATION of COLLOIDAL HARD SPHERES

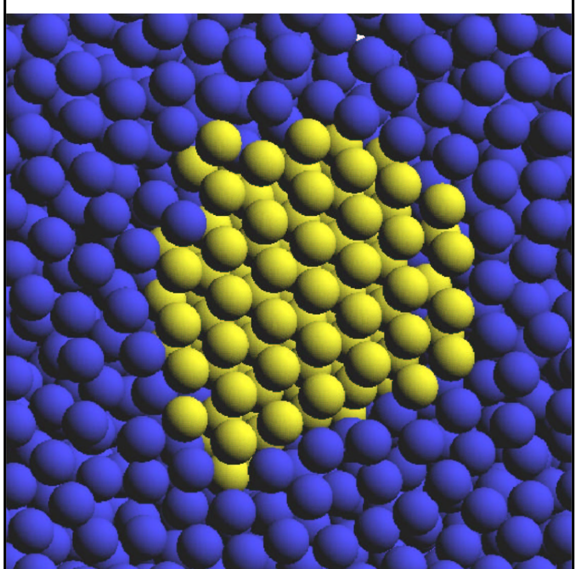
WHY THIS SYSTEM?

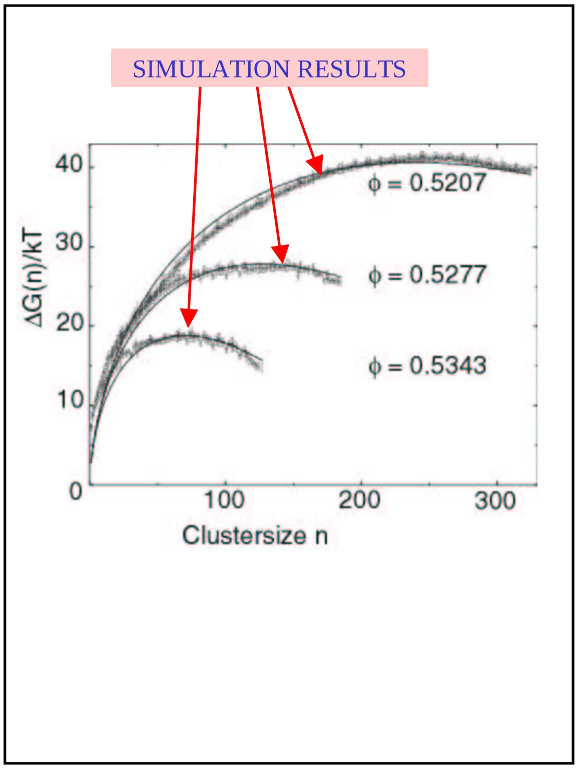
1. **We know "everything" about the equilibrium properties of hard spheres.**
2. **Suspensions of uncharged *silica* or *PMMA* colloids really behave like hard-sphere systems**
3. **There is experimental information on hard-sphere nucleation.**(Ackerson & Schaetzel, Harland & van Megen:on earth. Cheng, Zhu, Chaikin et al.: in µ-gravity)

Pusey and van Megen *Nature* **320** 340 (1989)

Nucleation in REAL

Hard-sphere Colloids





BEST FIT to Classical Nucleation Theory

SIMULATIONS:

Supersaturated: $\gamma_{eff} \approx$ **0.72 kT/σ²**

At coexistence: $\gamma \approx$ **0.62 kT/σ²**

Experiments: $\gamma \approx$ **0.5 kT/σ²**

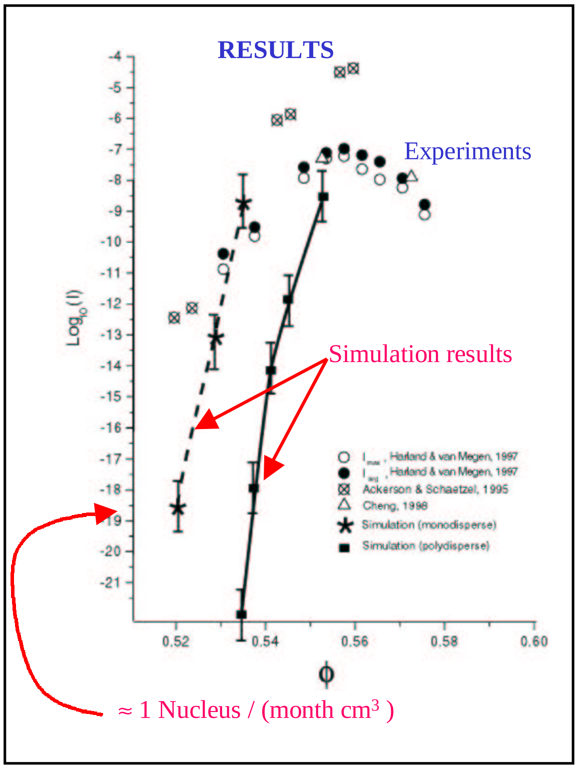
Some disagreement with CNT and with experimental estimates.

$$\Delta G^* \sim \gamma^3$$

Experiments underestimate barrier height by a factor 3 !

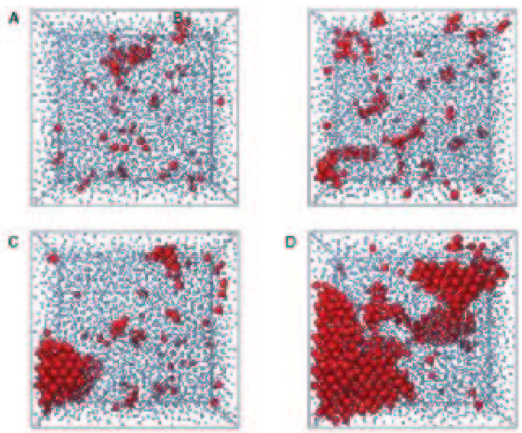
But remember, the nucleation rate is proportional to

$$\exp[-16\pi\gamma^3/(3\rho^2\Delta\mu^2 kT)]$$



Such disagreement is disastrous.

But wait, things get even worse…



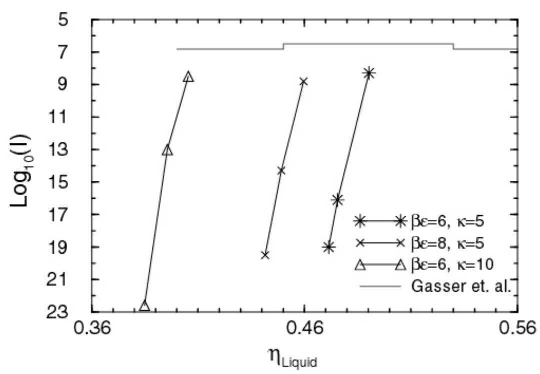
Confocal microscopy – Gasser et al. – Science, 292:258-262(2001))

Slightly charged colloidal spheres

Such experiments on provide DIRECT, MICROSCOPIC INFORMATION ON CRYSTAL NUCLEATION

Simulations and experiments disagree about:

1. **The structure of the nucleus**
2. **The interfacial free energy**
3. **The nucleation rate**



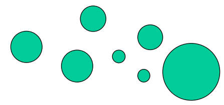
There's no success like failure…

(Bob Dylan)

A surprise:

THE EFFECT OF POLYDISPERSITY

POLYDISPERSITY IN HARD-SPHERE COLLOIDS

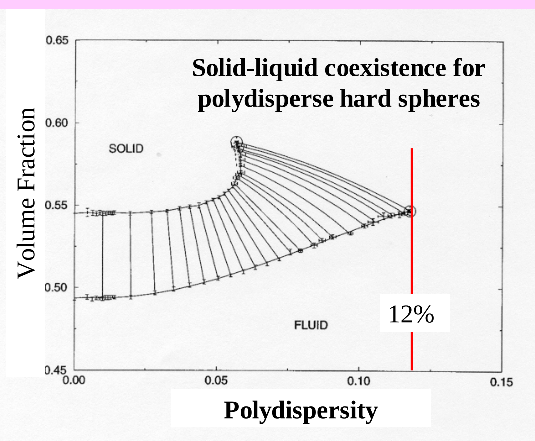


Polydispersity postpones, and eventually suppresses, hard-sphere freezing)

Polydispersity:

$$s \equiv (\langle r^2\rangle - \langle r\rangle^2)^{1/2} / \langle r\rangle$$

Phase diagram of polydisperse hard spheres



(Bolhuis & Kofke, PRE, 54:634(1996))

What does this imply for the behavior of the nucleation barrier?

$\Delta G^{*}=(16\,\pi/3)\gamma^{3}/(\rho\Delta\mu)^{2}$

Two "predictions":

1. **The barrier decreases**
2. **The barrier increases…**

Prediction 1

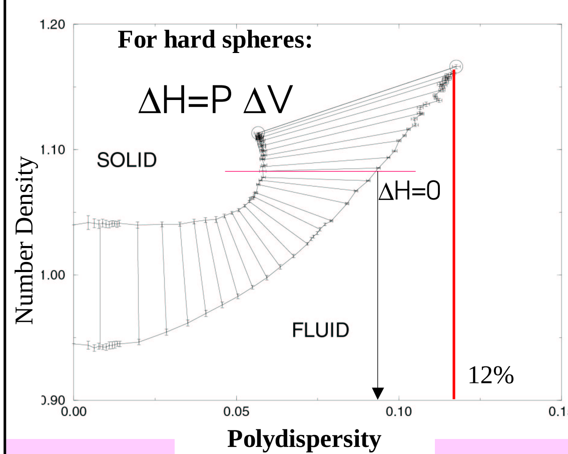
Use Turnbull's rule to estimate surface free energies (γ):

$$\gamma \approx 0.3 \;\; \Delta h/v^{2/3}$$

Where **Δh** is the enthalpy of fusion per particle, and **v** is the volume per particle (in the crystal)

"Turnbull's Rule"

$$\gamma = c \; \Delta H_s$$



Hence…

According to Turnbull, γ should go through zero, and hence the nucleation barrier

$\Delta G^* = (16\,\pi/3)\gamma^3/(\rho\Delta\mu)^2$

should vanish for polydispersities around 9%

Prediction 2

The "nucleation theorem" (Kashiev, Oxtoby, Viisanen, Strey, Reiss…) establishes a relation between barrier height and nucleus size:

$$\frac{\partial \Delta G}{\partial \mu} = -n^*$$

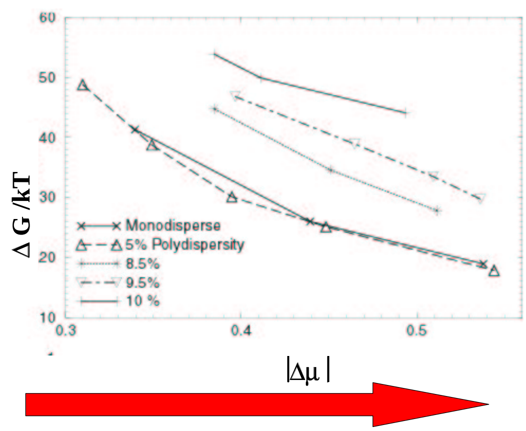
Where n^* is the excess number of particles in the critical nucleus

Hence:

When the number density of the critical nucleus is equal to that of the supersaturated liquid, then:

$$\frac{\partial \Delta G}{\partial \mu} = 0$$

What do the simulations say???



Increasing supersaturation

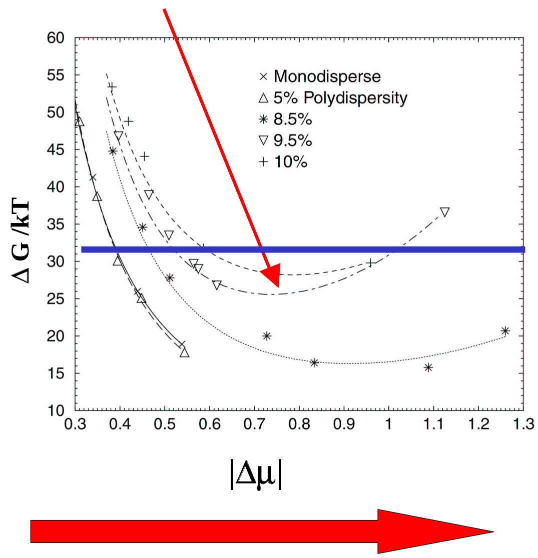
×	**monodisperse**
Δ	**5% polydispersity**
*	**8.5 %**
∇	**9.5 %**
+	**10 %**

Barrier INCREASES with polydispersity…

…also in the range where Turnbull's rule would predict that it should be zero!

Moreover…

It goes through a minimum!!!



Increasing supersaturation

Prediction 2 wins!

$$\frac{\partial \Delta G}{\partial \mu} = n^*$$

The simulations suggest that γ increases with $|\Delta\mu|$, e.g.:

$$\Delta G^* = \frac{16\pi\gamma_0^{\ 3}(1+a\Delta\mu)^3}{3\rho\Delta\mu^2}$$

SUMMARY:

- **To understand Nucleation, we need to study the Critical Nucleus.**
- **The structure of the critical nucleus is often NOT as predicted by CNT**
- **We find that the barrier height also differs from the CNT predictions…**
- **…and the rates disagree with the analysis of the available experiments**


In short: we need better experiments and better theories….
…or better simulations!